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Subject Quantitative Determination of "Product" in Waste Solution at Settling Pond

By W. Singlevich

To K. Z. Morgan

R.B.

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J.E. Wirth 11/27/44

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November 22, 1944

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To K.Z. Morgan

From W. Singlevich

SUBJECT: QUANTITATIVE DETERMINATION OF "PRODUCT IN WASTE SOLUTIONS AT SETTLING POND

Summary:

In an effort to find out exactly how much product was present in the settling pond at S-x, both from an economical as well as health hazard point-of view, a procedure was worked out (in cooperation with G. Johnson, Analytical Research Group; Bldg. 706-A) whereby a quantitative determination could be made for the product content in the waste liquors.

To insure against contamination interference in this experiment, all equipment and apparatus used were checked out of the stockroom as absolutely new and "unused" equipment.

A 5 liter sample of pond water was taken just in front of the inlet pipe to the pond. A 6 foot pole with a receiving vessel attached to one end of it facilitated the transfer of the test solution from the pond into a 3 gallon crock.

The pond water was allowed to settle in the 3 gal. crock for 24 hours; a small amount of "sludge" settled to the bottom. For the quantitative product test, a 3 liter (measured with a liter graduate) portion of the clear supernatant liquid was added to a 4 liter wax lined beaker. A lanthanum fluoride precipitation was then carried out, a modified standard LaF_3 precipitation for product analysis, and the volume of solution was reduced from 3 liters to 50 ml such that after removal of the excess La^{+3} another precipitation, using only 5 mgs. of La^{+3}, was feasible. The solution, containing product carried by 5 mgs. of La^{+3} was then mounted on a 22½ mm. diameter platinum plate, dried, and counted in a standard alpha chamber.

The result of the count showed alpha disintegration due to product at the rate of 250 d/m/3000 ml. or 0.083 d/m/cc. of waste liquor in the settling pond. The absorption loss due to presence of 5 mg of La^{+3} was about 15%, such that one could rely on at least an 80% accuracy of the above results.
(For details of the experimental procedures involved please refer to subsequent pages of this report)

Conclusions: 1.) A satisfactory procedure for the quantitative determination of product in waste liquors in the settling pond was established.
2.) On the basis of 1 test, alpha activity due to product in the pond water was found to be 0.083 d/m/cc.

Walter Singlevich
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Details of Experimental Procedure:

All equipment used was checked out new from the stockroom.

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Sampling: (Assisted by A. Greenwood, H.P. Group.)

Date: November 14, 1944
Time: 3:00 P.M.
Lauritsen No: H.P. 2.

Sample was taken just in front of inlet pipe to pond; solution transferred from pond to 3 gal. crock by 1 liter vessel attached to 6 ft. pole. 5 liters of pond water were taken and placed in a crock and covered with a porcelain top; this was shipped by H.P. truck to Room 34 in Bldg. 706-A.

Lauritsen Scope Readings at time of sampling:

Location:	mr/hr
Top bannister on walk, facing inlet pipe,	73
Bottom bannister on walk, facing inlet pipe,	60
Scope "flush" against covered crock with solution,	0
Cover on crock open; scope 9" from solution at top,	2

The pond water was allowed to set for 24 hours so that the small amount of sludge present settled to the bottom of the crock.

Analytical Procedure:

A 3 liter sample of the pond water (measured by a 1 liter graduate) was taken and placed in 4 liter wax-lined pyrex beaker. The following outlined steps were taken to isolate the product from all other interfering components present in the waste pond water:

1.) Added 300 mg. La^{+++} (.1 mg La^{+++} per ml. solution)
2.) Added 225 ml. conc (27N) HF. (To make solution 2N respect to HF) and stirred with automatic stirrer for $\frac{1}{2}$ hour. (Use polystyrene stirrer, "NOT GLASS".)
3.) Centrifugation:

The technique employed to separate the LaF_3 precipitate carrying product from the remainder of the solution in the beaker was as follows: 4 250 ml. centrifuge bottles were taken and test solution was poured into each bottle. The bottles were centrifuged for 20 minutes at 1600 R.P.M. in the standard clinical centrifuge, supernatant liquid poured off, and precipitate in bottom of bottle salvaged. Again test solution from the 4 L. beaker was added to the ppt. in the centrifuge bottles and centrifuged; this process was repeated until the entire 3 liters of test solution was separated into ppt. and supernatatant. The ppt. from 3 of the centrifuge bottles was throughly washed into the 4th. bottle; the total ppt. in the bottle was then washed into a clean 100 ml. platinum evaporating dish; IN-HNO_3-HF was used as the wash solution (to prevent solution of LaF_3 in water) in transferring ppt. from bottle to evaporating dish.

4.) Fuming:

5 ml. conc. sulfuric acid was added to the ppt. and washings in the evaporating dish. The solution was evaporated down and fumed; heat source was infra-red-ray lamp. This converted the La^{+++} to the sulfate; also drove off the HF.

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5.) Dissolving:

After evaporating to dryers and noting that no more fuming was taking place, the dish was cooled in air and water was added to dissolve the lanthanum sulfate (Solubility in cold water is 3.0 g. $La_2(SO_4)_3$ per 100 ml. of water). Difficulty was encountered in this step; the water did not dissolve all of the ppt. Therefore there was still some LaF_3 present, silica (reaction of HF with glass of centrifuge bottles), or both. On this basis an additional 3 ml. conc. H_2SO_4 was added and the ppt. was fumed again and dissolved after reaching the "dryness" step. Undissolved ppt. was still present, therefore, HF was added to remove the excess silica. Fuming with H_2SO_4 was again necessary; after reaching dryness the ppt. was found to dissolve in water almost completely. (make water 1N with respect to nitric acid).

6.) Centrifugation:

The solution was centrifuged again to insure against any interference due to solids present.

7.) Oxidation:

The supernatant from step 6 containing product in solution was oxidized from the 4 to the 6 state using 0.05 M potassium dichromate. The solution should be kept 2-5 N in HNO_3. There was 40 ml. of solution at this point; therefore adding 25 drops of 2N dichromate made the solution 0.05 M in dichromate. The solution was heated on a water both for 80 minutes at 80°C. Solution changed from colorless to orange-brown color at this point.

8.) Precipitation:

After oxidation of product to the 6 state, La^{+++} can be precipitated as the fluoride without carrying product. Accordingly, the test solution was made 2N in HF by adding 4 ml. HF. This precipitated the original 300mg of La^{+++} added; the product was in solution.

9.) Centrifugation.

---, Separation-Decantation:

The supernatant from step 9 was decanted into a clean centrifuge tube and the ppt. was discarded after 2 washings with 3 ml. portions of 1N HNO_3.

11.) Reduction:

The supernatant containing product in solution was subjected to a reduction step to reduce the product from the oxidized 6 state to the reduced 4 state. This was done by adding 2½ ml. of 2N hydrokylamine hydrochloride, making the 50 ml. of test solution 0.25 M with respect to $NH_2OH.HCl$. To bring about complete reduction, the solution should be allowed to set for at least 15 minutes after the original stirring.

The color of the solution at this point changed from orange-brown to blue-green.

12.) Precipitation:

The product in the original 3000 ml. volume has now been carried over to only a volume of 50 ml. The product was carried by a La^{+++} precipitation and made ready for mounting and counting.

A total of 5 mg. La^{+++} (.1mg. La^{+++} per ml. solution) was added to the test solution and made 2N with respect to HF by adding 4 ml. of 27 N HF. This was stirred with a polystyrene stirring rod for 5 minutes.

13.) Centrifugation:

The LaF_3 ppt. carrying product was separated from the supernatant by centrifuging for 20 minutes at 2100 R.P.M.

14.) Washing:

The small LaF_3 ppt. carrying product was then washed twice with 5 ml. portions of 1N HNO_3-HF solutions and was ready for mounting.

15.) Mounting:

A slurry of the ppt. and 1N HNO_3 was made (about 2 ml. total volume) by vigorus stirring with a polystyrene rod. The slurry was picked up by a syringe-pipette and mounted on a clean 22½ mm. diameter platinum plate.

The sample was dried under an infra-red-ray lamp and flamed in the flame of a bunsen burner.

16.) Counting:

The sample mounted on the platinum plate now contained only product carried by 5 mg. of La^{+++}. This sample was counted in a standard alpha chamber for 4 minutes. The average of 2 four minute counts was 134 cts. per minute. This 134 cts/min. was subject to a 52% geometry factor chamber, 4cts/min. background, and 12% absorption loss factor. Converting to disintegrations per minute, $\frac{134-4 \text{ cts./min.}}{.52}$ for 3 liters, or, $\frac{130}{3000 \times .52} = 0.083$ d/m/ml of water tested, neglecting absorption loss due to presence of 5 mg. of La^{+++}. The absorption loss due to lanthanum is 12.9% per mg. La^{+++} per cm^2 of surface; therefore, for 5 mg. it is 64.5% spread over 5.5 $cm.^2$ or $\frac{64.5}{5.5}$ = 11.8% absorption loss for this particular experiment.

In any event, the accuracy of this experimental result of 0.083 d/m/cc. water should not be off by more than 20%, as a liberal estimation.

Notes on test:

The entire experiment was conducted in Room 34, Bldg. 706-A where practically no alpha activity was present. There was, however, one experiment being conducted in the same hood as this particular test was in the evaporating stage. It is possible but not very likely that contamination via air currents and dust could have occurred, but certainly not in sufficient quantity to seriously affect the results obtained per this test.

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It is recommended that more work of this nature be carried out, particularly in checking how well results can be duplicated, product content of waste solution entering pond, content in the pond, and in the liquors leaving the pond.

Walter Singlevich

November 22, 1944

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